



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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| <b>(51) International Patent Classification <sup>5</sup> :</b><br><b>C08F 26/06, 26/10, 226/10</b>   | <b>A1</b> | <b>(11) International Publication Number:</b> <b>WO 92/07011</b><br><b>(43) International Publication Date:</b> 30 April 1992 (30.04.92)   |
| <b>(21) International Application Number:</b> PCT/US91/05239<br><b>(22) International Filing Date:</b> 24 July 1991 (24.07.91)<br><br><b>(30) Priority data:</b><br>599,592 18 October 1990 (18.10.90) US<br>628,122 17 December 1990 (17.12.90) US<br><br><b>(71) Applicant:</b> ISP INVESTMENTS INC. [US/US]; 818 Washington Street, Wilmington, DE 19801 (US).<br><br><b>(72) Inventors:</b> SHIH, Jenn, S. ; East 107 Prospect Street, Paramus, NJ 07652 (US). CHUANG, Jui-chang ; 110 Overlook Avenue, Wayne, NJ 07470 (US). SMITH, Terry, E. ; 143 Lake Road, Morristown, NJ 07960 (US). BIRES, Carmen, D. ; 35 Benington Square, Hackettstown, NJ 07840 (US). HELIOFF, Michael, W. ; 485 Otisco Drive, Westfield, NJ 07090 (US). LOGIN, Robert, B. ; 137 Page Drive, Oakland, NJ 07436 (US).  |           | <b>(74) Agents:</b> MAUE, Marilyn, J. et al.; GAF Corporation, Patent Dept., Bldg. 10, 1361 Alps Road, Wayne, NJ 07470 (US).<br><br><b>(81) Designated States:</b> AT (European patent), AU, BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent).<br><br><b>Published</b><br><i>With international search report.</i> |
| <b>(54) Title:</b> SWELLABLE, CROSSLINKED POLYVINYLPIRROLIDONE AND COSMETIC COMPOSITIONS THEREWITH<br><br><b>(57) Abstract</b><br><br>What is provided herein are strongly swellable, moderately crosslinked polyvinylpyrrolidone polymers in the form of fine, white powders characterized by (a) an aqueous swelling parameter defined by its gel volume of about 15 to 150 ml/g, (b) a Brookfield viscosity in 5 % aqueous solution of at least about 10.000 cps, and (c) being prepared directly by a precipitation polymerization process in an organic solvent, in the presence of about 0,2 to 1 % by weight of vinylpyrrolidone, of a multifunctional cross-linking agent, preferably about 0.25 to 0.8 %, and optimally, about 0.35 to 0.6 %. Those polymers in the amount of 0.2 to 10 % by wt. are included in cosmetic compositions for the care of hair and skin. |           |  |

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SWELLABLE, CROSSLINKED POLYVINYLPIRROLIDONE AND COSMETIC  
COMPOSITIONS THEREWITH

This invention relates to crosslinked polyvinylpyrrolidone (PVP), and more particularly, to strongly swellable, moderately crosslinked PVP polymers which are prepared directly as fine, white powders by precipitation polymerization of vinylpyrrolidone (VP), and to cosmetic compositions therewith.

Polyvinylpyrrolidone is made by homopolymerization of vinylpyrrolidone in bulk, solution or suspension. The polymer is obtained as (1) water soluble PVP; (2) water insoluble PVP which is variably swellable in water and which may form soft gels if strongly swellable.

(1) Water soluble PVPs usually are polymerized in aqueous solution using hydrogen peroxide. Polymerization also can take place in organic solvents such as methanol, isopropanol, toluene, benzene, tetrahydrofuran, acetone and hexane, usually with the production of lower molecular weight polymers than polymerization in water.

Belgian Patent 668,368, for example, disclosed a process for preparing homo- and copolymers of vinyl lactams in aliphatic hydrocarbons. However, the patent was limited to water soluble polymers and copolymers of vinyl pyrrolidone and vinyl caprolactam without crosslinking agents.

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(2) Water insoluble polymers of VP which are variably swellable may be prepared by copolymerizing VP in the conventional manner with or without difunctional vinyl or acrylic compounds acting as crosslinking agents. However, even when different amounts of the difunctional component was used, it was not possible to prepare polymers which were only slightly swellable in water.

U.S. Pat. 2,938,017, for example, disclosed that insoluble polymerization products can be obtained by heating VP alone, without the addition of water but in the presence of basic alkali or alkaline earth metal compounds such as the oxides, hydroxides or alkoxides of sodium or potassium. This method produced slightly swellable polymers, which, however, showed strong discoloration due to the high temperature at which polymerization took place. Moreover, the reaction was very difficult to control under these conditions.

U.S. Pats. 3,277,066 and 3,306,886 disclosed processes for the manufacture of insoluble PVP in which VP was placed in an autoclave and heated under pressure at about 140°C. in the presence of water and catalysts such as alkali metal hydrides, alkali metal borohydrides and/or alkali or alkaline earth metal hydroxides or alkoxides until the polymerization reaction had started. These processes also produced only sparingly swellable polymers with the disadvantage that elevated temperatures were required to start the polymerization reaction, and this necessitated the use of pressure vessels when water was included.

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German Patent No. 2,437,640 disclosed that VP can be polymerized in dilute aqueous solution in the presence of a crosslinking agent in the absence of oxygen and additionally in the presence of from 0.05 to 2% by weight, based on VP, of one or more ketocarboxylic acids or their methyl or ethyl esters. A small amount of a base was used concomitantly. However, polymerization at the high pH of the reaction caused yellowing of the polymers.

U.S. Pat. 3,933,766 described the preparation of insoluble PVP which was only slightly swellable by the so-called "popcorn" or proliferous polymerization technique. In this method, VP was polymerized to insoluble, slightly swellable, crosslinked PVP by heating an aqueous solution of VP in the presence of a bifunctional cyclic acid amide, but without any radical initiator, at about 80°-100°C.

U.S. Pat. 4,451,582 disclosed a process for the preparation of insoluble, particulate PVP polymers which were only slightly swellable in water. These polymers were obtained from basic vinyl heterocycles having a pKa higher than 4, and their copolymers, with as much as 30% by weight of copolymerizable monomers. The monomers were polymerized in the presence of from 0.1 to 10% by weight, based on the total amount of monomers, of a crosslinking agent, in the absence of oxygen and polymerization initiators. The polymers were preferably prepared by precipitation polymerization in water; however, they could be obtained in the absence of solvents for the monomers, by heating the latter to, preferably, 150°-180°C. This reaction was difficult to control and gave only low yields and relatively highly contaminated products.

U.S. Pat. 3,759,880 described a process in which VP was polymerized in aqueous solution in admixture with monomeric cyclic acid amides containing at least two ethylenically unsaturated groups of which at least one was attached to an amide nitrogen atom. The reaction was initiated in the presence of metals susceptible to attack by oxygen or in the presence of polymer seeds obtained from the monomers in the presence of such metals.

U.S. Pat. 4,647,637 disclosed a process for making insoluble PVP powders which were only slightly swellable by polymerization of VP and a crosslinking agent in a powder bed in the presence of a heat-transfer medium which was inert to the reactants, and in the absence of oxygen or polymerization initiator, at from 90° to 220°C., while maintaining the reactants in the powder state, circulating the reaction mass and evaporating the heat-transfer medium from the polymerization zone.

U.S. Pat. 2,658,058 disclosed a process for crosslinked linear PVP polymers by treatment of the polymer with hydrazine and hydrogen peroxide; U.S. 3,350,366 used *L, W*-diolefins and hydrogen peroxide; U.S. 2,658,058 used persulfate; and in J. Phys. Chem. 63, 1852 (1959), crosslinking was effected by irradiation.

U.S. Pats. 4,330,451 and 4,333,112 disclosed a post-treatment process for rendering PVP more highly viscous. In this process, PVP was subjected to a heat treatment in the presence of a water-insoluble peroxide and in the absence of oxygen. However, this process suffered from the disadvantage of requiring an additional step to produce the desired high-viscosity PVP, and this step was difficult to carry out reproducibly.

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Polymer J. 17 (1) p. 143-152 (1985), entitled "Polymers of N-Vinylpyrrolidone: Synthesis, Characterization and Uses", disclosed that slightly swellable, crosslinked PVP can be made by polymerizing VP chemically in aqueous solution with free radical initiators using various amounts of bifunctional monomers as crosslinking agents.

U.S. 3,669,103 described a process for preparing gels of lightly crosslinked PVP by aqueous, solution polymerization of VP in the presence of crosslinking agents. The reaction product was a coherent mass of gel which was evaporated to dryness and ground to provide a finely particulate product.

However, these and other processes did not provide strongly swellable, moderately crosslinked PVP polymers directly as fine, white powders which could be used to thicken aqueous and non-aqueous solutions effectively.

Accordingly, it is an object of this invention to provide strongly swellable, moderately crosslinked PVP polymers directly as fine powders by precipitation polymerization of VP in the presence of a predetermined amount of a multifunctional crosslinking agent and a free radical initiator in an organic solvent.

Yet another object of this invention is to provide strongly swellable, moderately crosslinked PVP polymer powders characterized by an aqueous gel volume of about 15-150 ml/g of polymer and a Brookfield viscosity in 5% aqueous solution of at least 10,000 cps.

Still another object of the present invention is to provide crosslinked PVP polymer powders which can show favorable white, fine powder formation during polymerization, and which can be made in a high solids content, and which provide clear solutions of high viscosities, and enhanced stability as measured by their retention of viscosity during storage at 50°C., and excellent salt tolerance.

The selection of components for hair and skin treating formulations presents numerous difficulties involving compatibility. Several hair treatment and shampoo formulations have been developed which aim to provide conditioning action during cleansing so as to leave the hair soft, manageable and lustrous and thus to eliminate a separate application of creme rinses or conditioning treatments. Problems arise from the limited compatibility of anionic detergents with commercial cationic conditioning agents which precipitate out of solution in shampoo formulations.

Shampoo formulations have employed conventional anionic surfactants such as sodium lauryl sulfate, ammonium lauryl sulfate, amine lauryl sulfates and sodium lauryl sulfate ethers which have been found to be incompatible with most cationic conditioning agents at effective concentration levels.

Additionally, reproducible thickening for formulations containing anionic detergents such as sodium  $\alpha$ -olefin sulfonates is very difficult to achieve.

Accordingly, it is another object of this invention to minimize or obviate the above problems while providing additional benefits in hair and skin treating formulations.

Another object of the invention is to provide cosmetic compositions containing strongly swellable, moderately crosslinked polyvinylpyrrolidone polymers which have excellent hair conditioning and thickening properties when incorporated into a shampoo and having high compatibility with components of hair and skin treating formulations.

Among the other objects herein is to provide a sunscreen lotion which is water-resistant.



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What is provided herein are strongly swellable, moderately crosslinked PVP polymers in the form of fine, white powders having (a) an aqueous gel volume of about 15 to 150 ml/g of polymer, (b) a Brookfield viscosity in 5% aqueous solution of at least about 10,000 cps, which (c) are prepared directly by precipitation polymerization of VP in the presence of a crosslinking agent in the amount of about 0.2 to about 1% by weight of VP.

In the preferred embodiment of the invention, (a) is 25 to 75 ml/g of polymer, (b) is at least 15,000 cps, and (c) is about 0.25 to 0.8%. In an optimum form of the invention, (a) is 30 to 60 ml/g, (b) is about 20,000 to 50,000 cps, and (c) is about 0.35 to 0.6%.

Gel volume is a measure of the swelling property of the crosslinked polymer and is defined as the equilibrium aqueous swelling volume of polymer per unit weight, and is expressed in the units of ml/g. Gel volume is determined by first adding 1 g. of the polymer to a suitable graduated cylinder filled with water. This mixture then is shaken and allowed to stand at room temperature for 3 days. The volume of the gel which is produced in water is measured and taken as the gel volume. Similarly, the gel volume concept can be applied to non-aqueous systems.

The fine, white powder polymers of the invention are prepared directly by a precipitation polymerization process in an organic solvent, such as an aliphatic hydrocarbon solvent, preferably cyclohexane or heptane, or an aromatic hydrocarbon, such as toluene, in the presence of about 0.2 to 1% by weight of VP of a crosslinking agent, preferably N,N'-divinylimidazolidone, triallyl-1,3,5-triazine-2,4,6(1H, 3H,5H)-trione 2,4,6-triallyloxy-1,3,5-triazine, and pentaerythritol triallyl ether at about 10 to 50% solids.

The cosmetic compositions of the invention are used particularly for the personal care of hair and skin, typically conditioning shampoos, lotions for the treatment of hand and body, and sunscreen formulations which are water-resistant.

#### DETAILED DESCRIPTION OF THE INVENTION

In accordance with the invention, strongly swellable, moderately crosslinked PVP polymers are prepared directly in the form of fine, white powders by precipitation polymerization of vinylpyrrolidone in the presence of a predetermined amount of a crosslinking agent and free radical polymerization initiator in an organic solvent, preferably an aliphatic hydrocarbon, e.g. a C<sub>3</sub>-C<sub>10</sub> saturated, branched or unbranched, cyclic or acyclic aliphatic hydrocarbon, and most preferably cyclohexane or heptane, or mixtures thereof.

The amount of solvent used in the process of the invention should be sufficient to dissolve an appreciable amount of the reactants and to maintain the copolymer precipitate in a stirrable state at the end of the polymerization. Generally, about 10 to 50% solids, preferably 15-30%, is maintained in the reaction mixture.

The precipitation polymerization process of the invention is carried out in the presence of a suitable free radical polymerization initiator. Suitable initiators include acyl peroxides such as diacetyl peroxide, dibenzoyl peroxide and dilauryl peroxide; peresters such as t-butylperoxy pivalate, tert-butyl peroxy-2-ethylhexanoate; peroxides such as di-tert-butyl peroxide; percarbonates such as dicyclohexyl peroxydicarbonate; and azo compounds

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such as 2,2'-azobis(isobutyronitrile), 2,2'-azobis(2,4-dimethylvaleronitrile), 1,1'-azobis(cyanocyclohexane), and 2,2'-azobis(methylbutyronitrile). Other initiators known in the art also may be used. A preferred initiator is the following:

Preferred  
Initiator

|                             |                               |  |
|-----------------------------|-------------------------------|--|
| t-Butyl peroxy-<br>pivalate | Atochem N.A.<br>(Lupersol 11) | Liquid; 75% active<br>in mineral spirits |
|-----------------------------|-------------------------------|--|

The amount of such initiator may vary widely; generally about 0.2-5.0% is used, based on the weight of total monomers charged.

The reaction temperature may vary widely; generally the reaction mixture is maintained at about 40°-150°C., preferably 60°-70°C., during the polymerization. Pressure usually is kept at atmospheric pressure, although higher and lower pressures may be used as well.

The reaction mixture should be stirred vigorously under an inert atmosphere, e.g. nitrogen, during the polymerization. A stirring rate of about 100-600 rpm in a 1-liter lab reactor is quite adequate to effect the desired polymerization and to keep the precipitate in a stirrable state during the polymerization.

Suitable crosslinking agents for use in the invention include such multifunctional compounds as the divinyl ethers of an aliphatic diol, e.g. the divinyl ethers of 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,7-heptanediol, 1,8-octanediol, 1,9-nonanediol, 1,10-decanediol, 1,11-unidecanediol, and 1,12-dodecanediol; as well as the divinyl ethers of

diethylene glycol, triethylene glycol, tetraethylene glycol, pentaethylene glycol, hexaethylene glycol, heptaethylene glycol, octaethylene glycol, nonaethylene glycol, decaethylene glycol and further polyalkylene glycols up to a molecular weight of about 6000. Other suitable crosslinking agents include 1,7-octadiene, 1,9-decadiene, 1,13-tetradecadiene, divinylbenzene, N-N'-divinylimidazolidone, and methylene bisacrylamide; acrylates such as polyethylene glycol diacrylate, trimethylolpropane triacrylate, propylene glycol diacrylate; allyl ether derivatives of polyhydric alcohols such as pentaerythritol triallyl ether; or polyhydric alcohols esterified once or twice with acrylic acid; triallylamine, tetraallylethylene-diamine, diallyl phthalate, and the like. Preferred crosslinking agents are the following: N,N'-divinylimidazolidone, pentaerythritol triallyl ether, triallyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione and 2,4,6-triallyloxy-1,3,5-triazine.

The precipitation polymerization process of the invention may be carried out by first precharging a suitable reactor with a predetermined amount of the organic solvent, for example, an aliphatic hydrocarbon solvent, and heating the solvent to a desired reaction temperature while stirring vigorously under an inert gas atmosphere. The initiator is then charged into the reactor. Then a solution containing selected amounts of vinylpyrrolidone monomer and the crosslinker material is admitted into the reactor over a period of time, generally about an hour or more, and preferably below the surface of the solvent. Then the reaction mixture is held for an additional period of time for polymerization to be completed. Finally, the mixture is cooled to room temperature. Filtering, washing with solvent, and drying provides the desired polymer in yields approaching quantitative. Alternatively, the reaction product may be dried directly to provide the polymer powders.

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The heterogeneous polymerization process of the invention in cyclohexane or heptane solvent provides the desired PVP polymer product as a fine, white powder, which precipitates readily, in quantitative yield, with substantially the same degree of crosslinking as the charge of VP monomer and crosslinking agent, in a smooth polymerization without excessive swelling of polymer during the course of the process. More particularly, the solvents of the invention are non-solvents for PVP and enable the polymerization to proceed in the presence of crosslinking agent without excessive building up viscosity of the reaction mixture during polymerization.

The present crosslinked polyvinylpyrrolidone polymers possess unique properties, among which is their ability to build viscosity, while simultaneously providing a hair and skin conditioning capability in cosmetic formulations containing anionic surfactants. These compounds are highly compatible with  $\alpha$ -olefin sulfonates and anionic surfactant salts conventionally employed in shampoos and skin lotions. Their compatibility is such that up to 5% by weight or more of the polymer compounds can be incorporated in the formulation, a characteristic which permits the formation of effective formulations as liquids or gels, and can be employed in shampoos, hair conditioners and lotions as an agent which incorporates thickening and conditioning qualities in one additive; thus eliminating the need for separate chemical components to accomplish these individual needs. Generally, the compounds of this invention are mixed with a standard formulation of shampoo, cream rinse, hand or body lotion or creams, sunscreen, etc., in an effective amount which ranges from between about 0.2 to about 10% by weight, preferably between about 0.5 and about 5% by weight, of the total formulation. The present compounds in concentrations up to 5% by weight show no tendency to precipitate after extended periods including periods up to 6 months or more.

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For incorporating into a standard formulation of shampoo, cream rinse, hand or body lotion, etc., the present product is dissolved in an inert solvent such as water, propylene glycol, ethanol, etc., and the solution in the desired amount is mixed into the formulation to provide a homogeneous liquid, gel, cream or lotion. Incorporation of the present product is usually affected at room temperature under atmospheric pressure and requires no special formulating technique. However, for certain formulations incorporation of the present product can be effected at temperatures up to about 85°C. Amphoteric-containing shampoo formulations are best prepared by initially preparing an aqueous solution of the polymer and the amphoteric surfactant and then adding the solution to the shampoo formulation.

The invention will be illustrated by reference to the following examples, which are given in parts by weight unless otherwise specified.

#### EXAMPLE 1

A 2-liter, 4-necked reaction vessel was equipped with a condenser, a constant speed mechanical stirrer, set at 170 rpm with a torque indicator and an anchor agitator having an open radius of 4 and 5/6 inches, an adaptor for admitting nitrogen, and a thermocouple connected to a temperature controller. The vessel was charged with 1000 g. of cyclohexane and heated to 65°C. during 30 minutes while purging with nitrogen. The reactor then was held at 65°C. for an additional 30 minutes. Then 520 microliters of t-butylperoxy pivalate (Lupersol 11, 75% active) polymerization indicator was added. Thereafter a solution of 250 g. of vinylpyrrolidone and 1.25 g. of N,N'-divinylimidazolidone crosslinking agent was introduced

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into the charged reactor over a period of 4 hours while stirring the contents. The feeding rate was about 1.0 ml./min. Then the mixture was heated to 85°C. over a half-hour and held at that temperature for another half-hour. Then the mixture was transferred to a 2-liter high pressure reactor and 1.0 g. of 2,5-dimethyl-2,6-di-(t-butylperoxy)hexane (Lupersol 101, 90% active) was added. The reactor was sealed and heated to 130°C. for 8 hours, cooled to room temperature, and the mixture was dried in a rotary evaporator. The polymer product was oven dried at 100°C. and vacuum dried at 90°C. for 16 hours of each. A quantitative yield of a crosslinked PVP polymer containing about 0.5% crosslinking agent was obtained.

#### EXAMPLES 2-10

The procedure of Example 1 was followed using various amounts of different crosslinkers with the following results.

TABLE I

| Ex. No. | VP,<br>Amount (g) | Crosslinker* | Crosslinker,<br>Amount (g) | % Crosslinker | ** Product<br>Yield (%) |
|---------|-------------------|--------------|----------------------------|---------------|-------------------------|
| 2       | 250               | DI           | 0.25                       | 0.10          | 96.0                    |
| 3       | 250               | DI           | 0.625                      | 0.25          | 100.0                   |
| 4       | 250               | DI           | 2.5                        | 1.00          | 100.0                   |
| 5       | 250               | PTE          | 0.25                       | 0.10          | 93.0                    |
| 6       | 250               | PTE          | 0.625                      | 0.25          | 92.0                    |
| 7       | 250               | PTE          | 2.5                        | 1.00          | 94.2                    |
| 8       | 250               | MBA          | 0.625                      | 0.25          | 87.0                    |
| 9       | 250               | MBA          | 1.25                       | 0.50          | 96.0                    |
| 10      | 250               | MBA          | 2.5                        | 1.00          | 100.0                   |

\* DI = divinylimidazolidone,

PTE = pentaerythritol triallyl ether and

MBA = methylene bisacrylamide

\*\* based upon VP used, by weight



EXAMPLES 11-12

The procedure of Example 1 was followed using heptane as solvent in place of cyclohexane. The feeding rate of the solution of vinylpyrrolidone in crosslinking agent was 0.50-0.55 ml./min. The results are shown in Table II below.

TABLE II

| <u>Ex. No.</u> | <u>VP,</u><br><u>Amount</u> | <u>Crosslinker</u> | <u>Amount</u> | <u>%</u>           | <u>Product</u>   |
|----------------|-----------------------------|--------------------|---------------|--------------------|------------------|
|                | <u>(g)</u>                  |                    | <u>(g)</u>    | <u>Crosslinker</u> | <u>Yield (%)</u> |
| 11             | 200                         | DI                 | 1.0           | 0.50               | 95.6             |
| 12             | 250                         | PTE                | 1.25          | 0.50               | 91.5             |

DI - Divinylimidazolidone

PTE - Pentaerythritol triallylether

EXAMPLE 13

The reactor of Example 1 was provided with the anchor agitator positioned in the middle of the reactor and extended to within 2 inches of the bottom of the reactor. Two dip tubes were connected to two metering pumps. The thus-equipped reactor then was charged with the solvent which filled the reactor to about 4 inches above the bottom of the dip tubes. In this procedure, the solution of VP and crosslinking agent was admitted into the reactor through the dip tubes to a position below the surface of the solvent. The effect of such subsurface feeding of monomer-crosslinker solution was to reduce build-up of viscosity of the polymer product during the polymerization, resulting in a smoother course for the process, particularly with respect to effective stirring of the reaction mixture.

Properties of Polymer of Invention

The strongly swellable, moderately crosslinked PVP polymer powders of the invention are characterized by its unique gel volume and viscosity, which properties enable the polymer to thicken aqueous and non-aqueous solutions effectively.

The viscosity of the polymer is defined by its Brookfield viscosity in cps, which is determined upon a 5% aqueous solution of the polymer at 25°C. by a standard analytical procedure using Model LTV and Spindle No. 4.

For maximum utility, it is desirable that the hydrated polymer exhibit a high gel volume and a high viscosity. With increasing crosslinking density in the polymer, the gel volume decreases and viscosity increases and then decreases, passing through a maximum. In the crosslinked polymer system of this invention, an effective thickener product is provided by including crosslinker in the reaction mixture at a suitable concentration of about 0.2 to 1.0 % by weight, based upon VP, preferably about 0.25 to 0.8%, and optimally, at about 0.35 to 0.6%. At this suitable amount of crosslinker loading, the crosslinked polymer product exhibits a gel volume of about 15 to 150 ml/g of polymer and a Brookfield viscosity of at least 10,000 cps. At the preferred crosslinker concentration, the gel volume is about 25 to 75 ml/g of polymer and its Brookfield viscosity is at least 15,000 cps. At the optimal amount crosslinker present in the reaction mixture, the polymer exhibits a gel volume of about 30 to 60 ml/g of polymer and a Brookfield viscosity of about 20,000 to 50,000 cps.

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The viscosity of the crosslinked polymer of the invention is particularly substantially independent of extended storage time even at 50°C., and of pH, and is tolerant of monovalent and multivalent salts in solution.

As an added feature of the invention, the residual VP monomer content of the polymers obtained herein is less than about 0.1% by weight. In aqueous based processes, in contrast, the formation of a gel mass during polymerization may trap considerable amounts of VP monomer in the polymeric gel network.

Examples of specific cosmetic formulations are presented as follows:

EXAMPLE 14

| <u>Ingredients</u> | <u>Parts by Weight</u> |
|--------------------|------------------------|
| <u>CREAM RINSE</u> |                        |
| Polymer of Ex. 1   | 2.0                    |
| polyquaternium* 11 | 2.0                    |
| etyl alcohol       | 2.0                    |
| emulsifying wax    | 2.0                    |
| citric acid        | to pH 4                |
| deionized water    | qs                     |
| fragrance          | qs                     |
| preservative       | qs                     |

HAIR CONDITIONER

|                             |         |
|-----------------------------|---------|
| Polymer of Ex. 1            | 4.0     |
| polyquaternium* 11          | 2.0     |
| PEG-8 Distearate            | 2.5     |
| mineral oil                 | 1.5     |
| lanolin alcohol             | 1.0     |
| stearic acid                | 1.0     |
| PPG-20 methyl glucose ether | 1.0     |
| hydrolized animal protein   | 0.25    |
| citric acid                 | to pH 4 |
| deionized water             | qs      |
| Germaben II                 | 1.00    |
| fragrance                   | qs      |

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| <u>Ingredients</u>             | <u>Parts by Weight</u> |
|--------------------------------|------------------------|
| <u>BLOW DRY STYLING LOTION</u> |                        |
| Polymer of Ex. 1               | 1.5                    |
| ethanol                        | 3.0                    |
| polyquaternium* 11             | 2.0                    |
| PEG-10 Castor oil              | 0.2                    |
| fragrance                      | 0.2                    |
| phosphoric acid                | to pH 6                |
| deionized water                | qs                     |
| Germall 115                    | 0.50                   |

|                                   |       |
|-----------------------------------|-------|
| <u>CONDITIONING HAIR SPRAY</u>    |       |
| Polymer of Ex. 2                  | 2.0   |
| ethanol                           | 75.51 |
| ethyl ester of PVM/MA** copolymer | 4.0   |
| 2-amino-2-methyl-1-propanol 99%   | 0.09  |
| fragrance                         | 0.2   |
| propellant                        | 20.0  |

\* the quaternized ammonium polymer formed by reacting dimethyl sulfate and a copolymer of vinyl pyrrolidone and dimethylamino methylacrylate

\*\* vinyl methyl ether/maleic anhydride

|                                 |      |
|---------------------------------|------|
| <u>CONDITIONING SHAMPOO (1)</u> |      |
| Polymer of Ex. 3                | 1.5  |
| dodecylpyrrolidone              | 0.6  |
| polyquaternium 11               | 0.5  |
| sodium laureth-4-phosphate      | 0.8  |
| ammonium lauryl sulfate         | 40.0 |
| silk protein                    | 0.25 |
| tetrasodium ethylenediamine     | 0.2  |
| tetra-acetic acid               |      |
| deionized water                 | qs   |
| colorant                        | qs   |
| fragrance                       | qs   |
| Germaben II                     | 0.50 |

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| <u>Ingredients</u>              | <u>Parts by Weight</u> |
|---------------------------------|------------------------|
| <u>CONDITIONING SHAMPOO (2)</u> |                        |
| Polymer of Ex. 1                | 1.5                    |
| polyquaternium 11               | 2.0                    |
| sodium lauryl sulfate           | 10.0                   |
| sodium lauryl sulfate ether     | 10.0                   |
| Tego betain C                   | 10.0                   |
| Kathon cg                       | 0.05                   |
| deionized water                 | qs                     |

|                             |     |
|-----------------------------|-----|
| <u>HAND AND BODY LOTION</u> |     |
| Polymer of Ex. 3            | 1.0 |
| preservative [Germaben IIE] | 1.0 |
| glyceryl stearate           | 2.5 |
| cetyl alcohol               | 3.0 |
| Alkamuls SMS                | 2.5 |
| Alkamuls 20                 | 2.5 |
| propyl paraben              | 0.1 |
| deionized water             | qs  |

|                             |     |
|-----------------------------|-----|
| <u>SUNSCREEN LOTION</u>     |     |
| Polymer of Ex. 3            | 2.5 |
| sorbitol                    | 6.0 |
| preservative [Germaben IIE] | 1.0 |
| glyceryl stearate           | 2.4 |
| stearic acid                | 1.5 |
| octyl dimethyl PABA         | 7.5 |
| benzophenone-3              | 2.5 |
| lanolin                     | 2.5 |
| deionized water             | qs  |

|                            |      |
|----------------------------|------|
| <u>MOISTURIZING LOTION</u> |      |
| Polymer of Ex. 4           | 2.0  |
| mineral oil 70 CTS         | 2.0  |
| stearic acid               | 3.0  |
| emulsifying wax            | 3.0  |
| Dimethicone* 200 CTS       | 1.5  |
| Carbomer 934**             | 0.15 |
| Oleth-20***                | 1.0  |
| triethanolamine 98%        | 1.0  |
| deionized water            | qs   |
| preservative               | qs   |
| fragrance                  | qs   |

\* a mixture of methylated siloxane polymers end-blocked with trimethyl siloxy units (dimethylpolysiloxane)

\*\* cross-linked polymer of acrylic acid

\*\*\* PEG ether of oleyl alcohol

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| <u>Ingredients</u>   | <u>Parts by Weight</u> |
|--|------------------------|
| <u>BUBBLE BATH</u>   |                        |
| Polymer of Ex. 5   | 3.0                    |
| ammonium nonoyno1-4-sulfate                                    | 30.0                   |
| sodium cocoyl isothionate                                      | 10.0                   |
| cocamidopropyl hydroxysultaine                                 | 10.0                   |
| cocamide diethanolamide  | 6.0                    |
| sodium methyl cocyl taurate                                    | 20.0                   |
| aloe vera gel  | 1.0                    |
| coconut oil  | 1.0                    |
| glycol stearate  | 1.0                    |
| deionized water  | qs                     |
| Germaben II  | 0.50                   |
| colorant   | qs                     |
| <u>SHAMPOO FOR OILY HAIR</u>                                   |                        |
| Polymer of Ex. 5   | 3.0                    |
| n-dodecylpyrrolidone   | 1.0                    |
| tetrasodium ethylenediamine                                    | 0.2                    |
| tetra-acetic acid  |                        |
| sodium lauryl sulfate  | 20.0                   |
| alpha-olefin sulfonate   | 20.0                   |
| polyquaternium 11  | 0.5                    |
| deionized water  | qs                     |
| Germaben II  | 0.50                   |
| colorant   | qs                     |
| fragrance  | qs                     |
| added inorganic salts as desired<br>for viscosity modification |                        |
| <u>SYNDET BAR (Superfatted)</u>                                |                        |
| Polymer of Ex. 6   | 0.5                    |
| stearic acid, triple pressed                                   | 32.00                  |
| kettle soap  | 9.80                   |
| sodiumcocoyl isethionate                                       | 49.00                  |
| sodium methyl cocoyl taurate                                   | 6.90                   |
| citric acid, 50% aqueous                                       | 0.60                   |
| titanium dioxide   | 0.20                   |
| fragrance  | 1.00                   |
| preservative   | qs                     |

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IngredientsParts by WeightWATER RESISTANT EMOLLIENT AFTER SUN LOTION

|                                     |       |
|-------------------------------------|-------|
| Polymer of Ex. 7                    | 3.0   |
| mink Oil, Light Fraction            | 11.00 |
| glyceryl stearate, self emulsifying | 1.00  |
| stearic acid                        | 2.50  |
| mineral oil and lanolin alcohol     | 2.00  |
| myristyl myristate                  | 3.000 |
| mineral oil                         | 10.00 |
| PVP/Eicosene copolymer              | 2.00  |
| triethanolamine                     | 0.70  |
| sorbitol                            | 3.00  |
| hydroxyethylcellulose               | 0.30  |
| distilled water                     | qs    |
| Germaben IIE                        | 1.00  |
| fragrance                           | qs    |

NON-ALCOHOLIC CONDITIONING MOUSSE

|                   |       |
|-------------------|-------|
| Polymer of Ex. 7  | 5.00  |
| polyquaternium 11 | 2.0   |
| Oleth-20          | 0.50  |
| fragrance         | qs    |
| deionized water   | 77.50 |
| propellant A-46   | 15.00 |
| Germaben II       | 0.50  |

SELF-HEATING AEROSOL SHAVING CREAM

(Used dual dispensing valve containing  
30 ml stearic acid and 11% hydrogen peroxide)

|                                 |       |
|---------------------------------|-------|
| Polymer of Ex. 1                | 2.00  |
| stripped coconut fatty acid     | 1.10  |
| sorbitol                        | 10.00 |
| stearic acid                    | 4.20  |
| PEG-40 soritan peroleate        | 2.00  |
| triethanolamine                 | 3.00  |
| potassium hydroxide             | 1.00  |
| potassium sulfite               | 9.00  |
| fragrance                       | 0.80  |
| butyrated hydroxy toluene (BHT) | 0.01  |
| butyrated hydroxy anisole (BHA) | 0.01  |
| deionized water                 | qs    |
| Germaben II                     | 0.50  |

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IngredientsParts by WeightCATIONIC MOUSSE HAND/BODY LOTION

(Used 85 Parts of the following formula  
to 15 parts propellant A-46)

|                                     |      |
|-------------------------------------|------|
| Polymer of Ex. 1                    | 0.50 |
| polyquaternium 11                   | 2.0  |
| acetylated polyoxyethylene lanolin  | 2.00 |
| ethoxylated lanolin alcohols        | 1.00 |
| glyceryl stearate, self-emulsifying | 5.50 |
| cetyl alcohol                       | 1.50 |
| mineral oil, 70 CTS                 | 1.50 |
| stearyl alcohol                     | 1.50 |
| glycerin                            | 3.00 |
| isopropyl myristate                 | 4.00 |
| dimethicone, 100 CTS                | 2.00 |
| water                               | qs   |
| preservative                        | qs   |
| fragrance                           | qs   |

AFTER SHAVE BALM

|  |      |
|--|------|
| Polymer of Ex. 1   | 1.00 |
| Carbomer 941   | 0.20 |
| tetrasodium ethylene diamine tetra-<br>acetic acid                     | 0.10 |
| cetearyl alcohol* and polyethylene<br>glycol ether of cetearyl alcohol | 2.50 |
| isopropyl myristate  | 1.00 |
| Oleth-20   | 1.00 |
| methyl gluceth 20  | 2.00 |
| triethanolamine, 98%   | 0.20 |
| propylene glycol   | 3.00 |
| SDA denatured alcohol  | 7.50 |
| PVP/dimethylaminoethyl methacrylate                                    | 7.00 |
| fragrance  | 1.00 |
| distilled water  | qs   |
| preservative   | qs   |

\* 50/50 mixture of cetyl and stearyl alcohols



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## WHAT IS CLAIMED IS:

1. Strongly swellable, moderately crosslinked PVP polymer in the form of fine, white powders characterized by (a) an aqueous gel volume of about 15 to 150 ml/g of polymer, (b) a Brookfield viscosity in 5% aqueous solution of at least about 10,000 cps, and (c) being prepared directly by precipitation polymerization of VP in the presence of a crosslinking agent in the amount of about 0.2 to about 1% by weight of VP.

2. A polymer according to claim 1 wherein said precipitation polymerization is carried out in an organic solvent.

3. A polymer according to claim 1 in which said crosslinking agent is selected from N,N'-divinylimidazolidone, pentaerythritol triallyl ether, triallyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione and 2,4,6-triallyloxy-1,3,5-triazine.

4. A cosmetic composition for the care of hair and skin containing about 0.2 to 10% by wt. of the polymer of claim 1.

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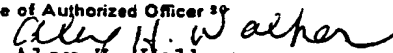
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5. A cosmetic formulation according to claim 4 wherein the cosmetic formulation is a shampoo and the amount of crosslinked polyvinylpyrrolidone is effective for conditioning hair.

6. A cosmetic formulation according to claim 4 which is a hand and body skin lotion, a water-resistant sunscreen lotion, a cream rinse, a hair conditioner, or a conditioning shampoo.

# INTERNATIONAL SEARCH REPORT

International Application No PCT/US91/05239

|  |  |                                     |
|--|--|-------------------------------------|
| <b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>1</sup>  |  |                                     |
| According to International Patent Classification (IPC) or to both National Classification and IPC<br>IPC (5): C08F 26/06, 26/10, 226/10<br>U.S. C1: 526/258, 264   |  |                                     |
| <b>II. FIELDS SEARCHED</b>   |  |                                     |
| Minimum Documentation Searched <sup>4</sup>  |  |                                     |
| Classification System <sup>1</sup>   | Classification Symbols   |                                     |
| U.S.   | 526/258, 264   |                                     |
| Documentation Searched other than Minimum Documentation<br>to the Extent that such Documents are Included in the Fields Searched <sup>5</sup>  |  |                                     |
| <b>III. DOCUMENTS CONSIDERED TO BE RELEVANT</b> <sup>14</sup>  |  |                                     |
| Category <sup>6</sup>  | Citation of Document, <sup>16</sup> with indication, where appropriate, of the relevant passages <sup>17</sup> | Relevant to Claim No. <sup>18</sup> |
| A,P  | US, A, 5,015,708 (SHIH ET AL) 14 MAY 1991<br>See the entire document.  | 1-3                                 |
| A  | US, A, 4,053,696 (HERRLE ET AL) 11 OCTOBER 1977<br>See the entire document.                                    | 1-3                                 |
| A  | US, A, 4,058,655 (DENZINGER ET AL) 15 NOVEMBER 1977<br>See the entire document.                                | 1-3                                 |
| A  | US, A, 2,831,836 (FORCHIELLI) 22 APRIL 1958<br>See the entire document.  | 1-3                                 |
| A  | GB, A, 1,049,027 (FARBENFABRIKEN BAYER AKTIENGESELLSCHAFT) 23 NOVEMBER 1966; See the entire document.          | 1-3                                 |
| <div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p><sup>15</sup> Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p> </div> </div> |  |                                     |
| <b>IV. CERTIFICATION</b>   |  |                                     |
| Date of the Actual Completion of the International Search <sup>1</sup>   | Date of Mailing of this International Search Report <sup>2</sup>   |                                     |
| 14 NOVEMBER 1991   | 25 NOV 1991  |                                     |
| International Searching Authority <sup>1</sup>   | Signature of Authorized Officer <sup>19</sup>  |                                     |
| ISA/US   | <br>Alex H. Walker         |                                     |

Form PCT/ISA/210 (second sheet) (May 1986)

## FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE<sup>1</sup>

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers \_\_\_\_\_, because they relate to subject matter not required to be searched by this Authority, namely:
  
2. ☐ Claim numbers \_\_\_\_\_, because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out<sup>2</sup>, specifically:
  
3. ☐ Claim numbers \_\_\_\_\_, because they are dependent claims not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. ☒ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING<sup>2</sup>

This International Searching Authority found multiple inventions in this international application as follows:

- I. Claims 1-3 a crosslinked polyvinylpyrrolidone.
- II. Claims 4-6 a cosmetic composition.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all the claims of the international application.
2. ☒ As only some of the required additional search fees were timely paid by the applicant, this international search report covers those claims of the international application for which fees were paid, specifically claims: 1-3
3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report does not cover the invention first mentioned in the claims; it is covered by claim numbers:
4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority invites payment of any additional fee.

## Remark on Protest

- ☐ The additional search fees were accompanied by applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.